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Acurex Corp., Research Triangle Park, NC

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16. ABSTRACT

The paper gives results of a characterization of post-furnace injection solids and flyash mixtures and their testing in a bench-scale reactor for the removal of SO2. Virtually no SO2 removal was observed with untreated solids. High SO2 capture occurred when the samples were hydrated and dried prior to SO2 exposure. The SO2 capture by solids increased with increasing time and temperature of hydration. For the same time/temperature conditions of hydration, higher SO2 capture was achieved with solids of higher flyash/sorbent ratio. A possible mechanism of enhanced SO2 capture by hydration of the product solids is discussed.

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Sulfur Dioxide	Coal	Stationary Sources	07B	21B
Limestone	Combustion	Characterization	08G	
Sorbents	Furnaces		11G	13A
Fly Ash			21B	
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Reactivation of Solids from Furnace Injection of Limestone for SO_2 Control

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■ Post furnace injection solids and fly ash mixtures were characterized and were tested in a bench-scale reactor for the removal of SO_2. Virtually no SO_2 removal was observed with untreated solids. High SO_2 capture occurred when the samples were hydrated and dried prior to SO_2 exposure. The SO_2 capture by solids increased with increasing time and temperature of hydration. For the same time/temperature conditions of hydration, higher SO_2 capture was achieved with solids of higher fly ash/sorbent ratio. A possible mechanism of enhanced SO_2 capture by hydration of the product solids is discussed.

Introduction

The direct injection of calcium compounds into coal-fired furnaces/boilers for controlling SO_2 emissions has been of environmental interest for some time because of its relatively low capital cost. Recent studies discuss the potential of this control technology (*1*) and also report on efforts to understand the mechanism of SO_2 capture in the furnace (*2*, *3*). If proven economically attractive for meeting mandated SO_2 control levels, direct injection of limestone into the furnace could become the predominant means of reducing the emissions of SO_2 from the combustion of coal. However, the low sorbent utilization makes potential operating costs and SO_2 capture less attractive. For example, during tests at Du Pont's Martinsville, VA, plant, the limestone utilization (percentage of sorbent that actually reacts with SO_2 to form sulfite/sulfate products) was 18–20% with 50% SO_2 removal at stoichiometric ratios of 2.75–2.5 (*4*). Higher sorbent utilization leading to lower stoichiometry and more effective SO_2 removal is needed to make this control technology competitive with commercial flue gas desulfurization systems.

The highest apparent limestone utilization during the 1981 tests at Hoot Lake Station was 15% at a ratio of calcium in the limestone to the sulfur in the lignite (stoichiometry) of 2, with SO_2 removal of 27–29% at average flue gas SO_2 concentrations of 640–700 ppm (*5*). Maximum SO_2 removal was 47%, but at this removal the utilization was only 9% for a stoichiometry of 5 and an average SO_2 concentration of 630 ppm (*6*). Utilization was described as the ratio of moles of sulfur captured to the moles of calcium injected into the boiler. These results differed greatly from the test goal of at least 50% SO_2 removal at a stoichiometry of 2. To satisfy this goal, additional removal of SO_2 would be needed between the boiler and the stack, with the most apparent location for additional SO_2 removal being in the duct from the boiler to the particulate control device and in the device itself.

Improved SO_2 removal may be enhanced by injecting highly reactive solids into the boiler/furnace. This approach was suggested in papers reporting Department of Energy (DOE) supported work at the University of North Dakota Energy Research Center (*6–8*). These researchers proposed that pressure-hydrated dolomitic or calcitic lime in place of limestone be injected into the boiler and that a more reactive sorbent could be produced by doping the raw material with sodium in the pressure hydrator.

While in the boiler/furnace, the injected solids will react with other materials to form gaseous and solid products. These reactions may activate certain compounds that combine with SO_2. For example, the thermal environment in the boiler/furnace leads to some calcination of limestone, and the resulting lime may react with SO_2. The fly ash formed during combustion may contain alkaline material, depending on the coal fired, which can also capture SO_2 in the boiler/furnace. The foregoing reactions will unlikely go to completion because of reagent blinding or other inhibiting effects. Consequently, potential sorbents may be made available from inactivated materials (products) leaving the boiler/furnace. These products contain unreacted limestone, lime formed by calcination in the boiler, sulfated sorbent, and fly ash. If these products, which under normal conditions are considered to be wastes, could be reactivated to absorb SO_2 during its residence time in the duct and particulate control device, the resulting sorbent would improve SO_2 capture of the boiler limestone injection process. Increased sorbent utilization through reactivation of these products and their use in a dry sorbent injection process would beneficially use large quantities of normally wasted material.

The primary objective of this paper is to report the laboratory evaluation of the potential for the reactivation and reuse of boiler limestone injection solids (BLIS) for increasing the overall SO_2 capture and limestone utilization in both new and retrofitted control applications. The secondary objective is to propose a possible mechanism for the enhanced SO_2 capture obtained through the hydration of the product solids from the boiler/furnace and the subsequent in-duct injection of these dried solids into the flue gas between the boiler/furnace and particulate collector.

Principle of Reactivation

Previous studies (*8*) have shown that hydration of fly ash and $Ca(OH)_2$ under favorable time/temperature conditions can enhance the utilization of lime and/or increase the capture of SO_2, as compared with $Ca(OH)_2$ alone. The main factor for enhanced SO_2 capture is the pozzolanic reaction on combining the boiler limestone injected solids (BLIS) and water with the activation process hypothesized as follows. In the reaction, silica and alumina are digested from fly ash under favorable conditions of time/temperature and high alkalinity. Next, nuclei of calcium silicates are formed and, after sufficient growth, precipitate on the surface of fly ash. For BLIS, the pozzolanic system is CaO–$CaSO_4$–fly ash–H_2O and $CaCO_3$. Apparently, the dissolution of silica and/or alumina is the rate-limiting step, with dissolution of alumina being faster than that of silica (*10*, *11*). The formation of calcium silicate hydrates in this process is temperature dependent, and at 38 °C these hydrates were common after 8 h of reaction (*12*).

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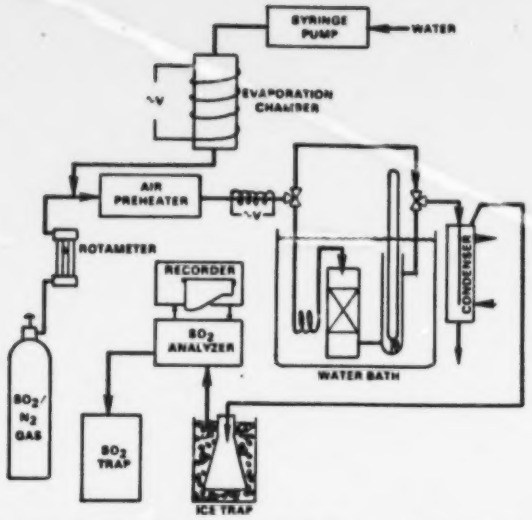


Figure 1. Experimental apparatus (sand bed reactor) for evaluating sorbent reactivity.

However, their formation usually begins within several minutes after the reaction starts. The $CaO–Al_2O_3–SiO_2–CaSO_4–H_2O$ system yields cementitious phases, which originate from the pozzolanic reaction of lime with fly ash or clay, and these phases may be hydrated calcium silicate of an ill crystallized nature ($CaO·SiO_2·H_2O$), tetracalcium aluminate hydrate ($4CaO·Al_2O_3·13H_2O$), hydrated gehlenite ($2CaO·Al_2O_3·SO_4·8H_2O$), ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$), and tetracalcium aluminate monosulfate ($3CaO·Al_2O_3·CaSO_4·12H_2O$) (*13*). These highly hydrated products have extremely high surface area, on the order of several hundred square meters per gram for fibrous gels of calcium silicate hydrates (*14*).

Fly ashes, especially high calcium fly ashes, have long been recognized as having pozzolanic properties (i.e., lime and water combining to form cementitious products of high surface area) (*15*). The reactivity of fly ash toward lime is favored by elevated temperature, grinding, and certain additives that chemically attack and dissolve the glassy outer layer of fly ash and thus increase the formation rate of cementitious products with high surface area (*16*). Since typical BLIS contain CaO, $CaSO_4$, $CaCO_3$, and fly ash, its reactivity might also be enhanced by hydration and pozzolanic reactions similar to those of its components.

Experimental Procedures

Apparatus. The reactivity of the BLIS samples was evaluated in a "sand bed reactor" (Figure 1) designed to simulate fabric filter operating conditions (*17*, *18*). An analysis of SO_2/sorbent reaction steps in the sand bed excluded diffusion of gaseous SO_2 to the surface of the sorbent and considered diffusion of SO_2 through the "ash" layer or reaction of SO_2 with the sorbent at the core as the rate-controlling step (*19*). The glass reactor (45 mm in diameter, 150 mm in length) was packed with powdered reagent mixed with 70-mesh silica sand to prevent channeling of sorbent. (See Table I for conversions from metric to British Engineering units.) The sand-to-reagent ratio ranged from 20:1 to 40:1. The reactor was immersed in a water temperature-controlled bath. Span gas served as the simulated flue gas. Water was metered by a syringe pump, vaporized at about 180 °C, and injected into the dry gas to control the humidity. Tubing upstream of the reactor was heat traced to prevent the condensation of the water vapor. Before entering the SO_2 analyzer, the gas was cooled and its water vapor condensed by an ice bath. The amount of condensed water vapor was measured to check the value of the relative humidity determined from wet- and dry-bulb thermometers.

Table I. Conversion of Metric to British Engineering Units

to obtain	from	multiply by
in.	mm	0.03937
ft^3/min	L/min	0.0353
lb/$in.^2$	Pa	1.4504×10^{-4}
ppm SO_2	g of SO_2/m^3	381.68
°F	°C	1.8 and add 32

SO_2 Absorption Test Procedure. The SO_2 concentration was measured continuously during each test. A bypass of the reactor permitted conditioning of the bed. Prior to each run, the bed was humidified for 1 h by passing pure nitrogen at the relative humidity at which the experiment was to be performed. Most of the experiments were performed at a relative humidity of 60% with some experiments at 30%. These relative humidities correspond to a 10 and 21 °C approach to saturation, respectively, in a spray dryer or fabric filter. Reactor dry-bulb temperature was controlled at 64.4 °C for both humidities. Common purity (99.5%) nitrogen was the conditioning gas, its flow rate being 4.7 L/min (0 °C, 101.3 kPa). The nominal SO_2 concentration was 500 ppm (1000 or 2000 ppm occasionally, previously reported sand bed tests on calcium and sodium sorbents showed SO_2 removal and sorbent utilization to be independent of inlet SO_2 concentration), and exposure time of the sample to the gas was 1 h. The exposure time of 1 h was selected as being representative of the solids residence time in the cake of a fabric filter, typical baghouse cleaning cycles ranging from 0.5 h to several hours or more depending on solids loading and characteristics as well as flow conditions and filter material.

Hydration Procedure. Sample preparation consisted of slurrying 10 g of BLIS as received at a water-to-solids ratio of 15:1 and stirring the slurry at a controlled temperature. Mixing time varied from 0 to 48 h at a slurry temperature of 25–90 °C. All hydrations were made at atmospheric pressure. After mixing, the samples were vacuum filtered and microwave dried for about 5 min to rapidly stop the hydration. During earlier work (*9*), oven drying was used instead of microwave drying. The degree of activation, as indicated by BET surface area, was the same for both oven and microwave drying, with the latter requiring half the time.

Sample Characterization. Six different samples of BLIS, produced in 1981 limestone injection experiments (*5*), were received from the Department of Energy (DOE). The characterizations of these samples are given in Table II. The available percent of CaO was determined by titration with 0.5 N hydrochloric acid against a phenolphthalein end point after the solubilization of $Ca(OH)_2$ with sugar [sugar increased the solubility of $Ca(OH)_2$ via the formation of calcium saccharate]. Insoluble solids were determined after 0.5 g of sample was slurried with 200 mL of deionized water and digested with 3–5 mL of concentrated HCl. The values of total Ca^{2+}, Mg^{2+}, and Na^+ were obtained by atomic absorption, and that of SO_4^{2-} was by ion chromatography (Dionex 14). Particle size analysis was done on a Microtrac analyzer (Leeds & Northrup 7991-01 particle size analyzer). The morphology of the samples was characterized on an Amray scanning electron microscope (SEM). The composition of the particles was measured by a PGT1000-XCEL system from Princeton Gamma

Table II. Characterization of BLIS from Hoot Lake Station

BLIS sample	mean diameter, μm[a]	BET surface area, m^2/g	available CaO, %[b]	insoluble solids, %[b]	fly ash loading, g/g[c]	$CaSO_4$, %[b]	Mg, %[b]	Na, %[b]	total Ca, %[b]
1	13.5	2.67	14.6	26	1.78	12	6	4	37
2	13.9	1.36	14.0	20	1.43	12	6	4	35
3	12.0	1.48	6.9	29	4.20	12	7	6	33
4	13.5	1.66	20.0	23	1.15	10	4	3	49
5	12.9	1.12	5.5	27	4.91	10	7	4	37
6	16.8	1.74	6.0	35	5.83	10	7	9	40

[a]Diameter is based on measured volume and assumed spherical particle. [b]Percentage is based on weight. Other analyses required to permit components to total 100% were not available. [c]Fly ash loading is the ratio of fly ash to calcium oxide.

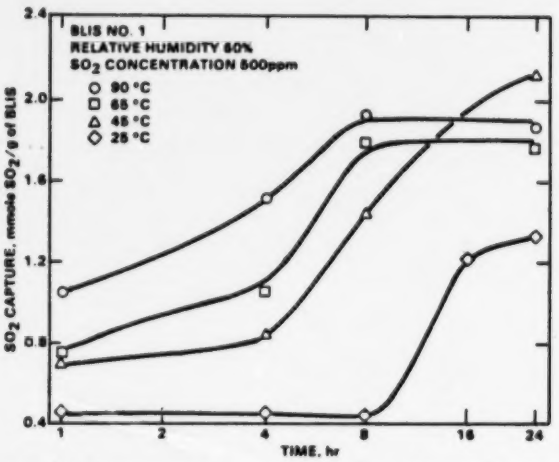


Figure 2. Effect of time/temperature conditions of hydration on the SO_2 capture by BLIS in the sand bed.

Tech, while the crystalline phases were detected with an X-ray diffractometer. The nitrogen BET surface area was determined on an Accusorb 2100 from Micrometrics. The characterization of solids from experimental batches of sorbents is given in Table III.

Results and Discussion

Untreated BLIS. To evaluate the potential of untreated BLIS for SO_2 removal downstream of the boiler, the samples were tested with the procedure described earlier. The results showed that virtually no SO_2 removal occurred with the BLIS as received: 3% removal in the case of BLIS 1 and 5% removal in the case of BLIS 6. Since the untreated BLIS did not capture SO_2, hydrating the solids at elevated temperature for a prolonged period of time was tried as a means of activating these solids.

Effect of Hydration. The effect of hydration time/temperature on the reactivity of hydrated BLIS 1 is shown in Figure 2. The reactivity is represented by the SO_2 capture, defined as the number of millimoles of SO_2 captured by 1 g of sorbent during the 1-h exposure to SO_2 in the sand bed. Figure 2 also shows that the SO_2 capture increased with temperature of hydration and was monotonically nondecreasing with hydration time.

For the samples hydrated at 65 and 90 °C over 1–8-h intervals, the SO_2 capture increased with time of hydration but leveled off at about 1.8 mmol of SO_2/g after 8 h. Because of the difference in trends for SO_2 capture for hydration at 45 °C and that at 65 and 90 °C, the test for SO_2 capture with BLIS 1 hydrated for 24 h at 45 °C was repeated. The earlier result was confirmed that SO_2 capture by BLIS reactivated by hydration over 24 h at 45 °C exceeded that at 65 and 90 °C. While this may be due to the formation of a more active phase at 45 °C than at 65 or 90 °C, no further analytical evidence has been gathered to support this hypothesis. This hypothesis may be evaluated in the future. Hydration times greater than 8 h were needed to activate samples held at 25 °C. The SO_2 capture by solids hydrated at this temperature was 0.45 and 0.42 mmol of SO_2/g after hydration for 1 and 8 h, respectively.

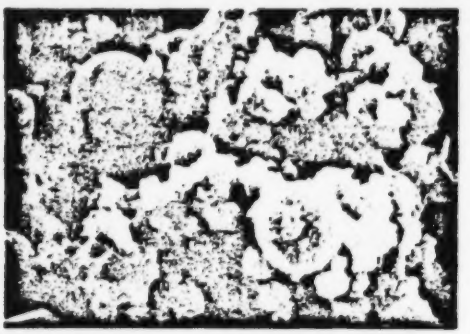


Figure 3. SEM photograph of untreated BLIS 1 (3000×).

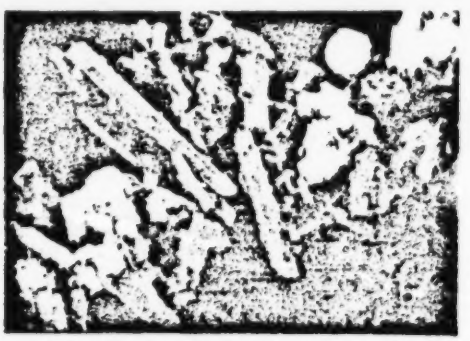


Figure 4. SEM photograph of BLIS 1 hydrated at 90 °C for 4 h (3000×).

Two experiments were performed at zero time, when water at a desired temperature was poured over dry solids and mixed for about 2 min before vacuum filtering and microwave drying. The SO_2 capture by solids prepared in this way was 0.53 and 0.68 mmol of SO_2/g when 65 and 90 °C water, respectively, was used. These results correlate well with those presented by Conoco researchers (*20–22*), who found wetting of the solid particles (following limestone injection into the boiler) a prerequisite for significant SO_2 capture, if one assumes that collisions between solid and water particles led to the formation of a moisture layer sufficient to wet the solids in the flue gas duct in the Conoco tests.

The morphology of the hydrated and unhydrated samples was characterized by SEM. Figure 3, a SEM photograph of an unhydrated sample of BLIS 1, shows the deposit of dead-burned lime/limestone on the surface of fly

Table III. Experimental Data (10 g of BLIS Hydrated with 150 mL of H_2O, SO_2 Concentration = 500 ppm, and Relative Humidity = 60%, unless Otherwise Noted)

expt no.	BLIS	hydration temp, °C	hydration time, h	BET surface area, m^2/g	available $Ca(OH)_2$, wt %	SO_2 capture, mmol of SO_2 g^{-1}
59	1	65	4	7.95	16.10	1.06
60	1	90	4	18.14	11.80	1.52
63	1	25	4	3.47	15.20	0.46
64	1	90	1	7.19	17.20	1.04
65	1	65	1	4.14	15.40	0.78
66	1	90	8	25.84	8.81	1.94
68	5	65	4	5.66	6.69	0.74
70	6	65	4	12.56	4.86	1.06
72	1	65	8	17.09	16.20	1.79
73	1	25	1	4.53	15.50	0.45
74	1	65	24	24.57	9.70	1.73
76[a]	1	90	4	22.62	11.10	1.68
78	2	65	4	9.42	16.32	1.37
79	3	65	4	4.99	7.28	0.73
80	4	65	4	5.70	20.82	1.01
81	1	25	24	9.29	11.97	1.32
82	1	90	24	50.86	8.14	1.84
83	1	65	4	8.46	15.69	1.24
87	1	65	"0"	4.69	16.21	0.53
88	1	90	"0"	5.57	16.31	0.68
91[a]	1	65	4	16.14	n/a	1.66
92	1	25	16	6.61	13.70	1.22
93	1	45	4	6.55	13.30	0.83
94	1	45	1	5.48	n/a	0.70
95	1	45	8	9.12	14.95	1.45
97	1	25	8	4.73	14.52	0.42
98	1	45	24	19.30	n/a	2.15
100[c]	1	25	4	13.36	11.65	1.33
101[b]	1	65	4	7.95	16.10	0.25
105[a,b]	1	65	4	16.14	n/a	0.27
106[b]	1	90	24	50.86	8.14	0.77
108[c]	1	65	4	7.95	16.10	0.96
109[c]	1	90	24	50.86	8.14	1.84
111	1	25	48	10.92	10.64	1.68
136[a,c]	1	65	4	16.14	n/a	1.72
137[a,c]	1	90	4	22.62	11.10	1.96

[a]Three weight percent of $(NH_4)_2HPO_4$ was added. [b]Relative humidity in the sand bed was 30%. [c]SO_2 concentration was 1000 ppm.

ash particles. The SEM photograph of a sample of BLIS 1 hydrated at 90 °C for 4 h in Figure 4 reveals crystals of a few micrometers in length, as well as the greatly enhanced surface of fly ash particles. X-ray elemental analysis of these "long crystals" gave peaks of Al, S, and Ca, which suggest that these crystals are ettringite or other synthetic calcium aluminate sulfates. This assumption was later confirmed by X-ray powder diffraction analyses, which detected $3CaO·Al_2O_3·CaSO_4·12H_2O$ and/or $3CaO·Al_2O_3·CaSO_4·13H_2O$ [Joint Committee on Powder Diffraction Standards (JCPDS) nos. 18-275 and 11-197], respectively, in the sample hydrated for 4 h at 90 °C. Peaks of the same spacing were found in the samples hydrated at 90 °C for 0, 4, and 24 h, but they were not detected in the 1-h hydrated sample. The normalized height of the peak increased from 53 for the 4-h hydrated sample to 83 for the 24-h sample (height normalized against highest peak). The increase in the intensity (amount) of synthetic calcium aluminate sulfate corresponds to the increase in the BET surface area and subsequent SO_2 capture in the sand bed reactor (i.e., the increased BLIS slurrying time led to greater calcium aluminate sulfate formation and higher SO_2 capture by the corresponding sorbent in the reactor). These peaks were not present in any of the BLIS received from the DOE. There was also a strong (normalized height of 30) peak of $Ca(OH)_2$ (JCPDS no. 4-733) in the 1-h hydrated sample but it was absent in the 24-h sample. Other peaks present (in both samples discussed) were $CaSO_4$ (JCPDS no. 6-226) and $CaCO_3$ (JCPDS no. 5-586). An ettringite peak of very high intensity (normalized height of 56) was detected in a sample hydrated at 45 °C for 48 h. In this sample, ettringite [$3CaO·Al_2O_3·3CaSO_4·31H_2O$] (JCPDS no. 9-416) and limestone ($CaCO_3$) were the only peaks found. Ettringite peaks were found in samples hydrated at 90 °C for "0" and 1 h, but they were absent in samples hydrated at the same temperature for 4 and 24 h. This finding suggests, consistent with observations after all gypsum available in the solution is consumed, that ettringite decomposes to form other calcium aluminate sulfates (*10*).

To further increase the SO_2 capture by BLIS, ammonium phosphate [$(NH_4)_2HPO_4$] was tested as an additive. The ammonium phosphate was reported to be capable of breaking the glassy layer on the surface of fly ash particles (*23*) so that the dissolution of silica/alumina compounds was facilitated; it had its most pronounced effect on the reactivity of BLIS hydrated at low temperature. The addition of 3% (by weight) of $(NH_4)_2HPO_4$ tripled the SO_2 capture by the sample hydrated for 4 h at 25 °C from 0.46 to 1.33 mmol of SO_2/g of BLIS. At 90 °C, with all other conditions the same as before, the SO_2 capture increased less dramatically (about 10%) from 1.52 to 1.68 mmol of SO_2/g of BLIS.

Parametric Tests. Parametric tests were also performed to study the effect of fly ash loading, SO_2 concentration, and relative humidity on the SO_2 capture by hydrated BLIS. The effect of fly ash loading on the SO_2 capture by BLIS hydrated at 65 °C for 4 h is shown in Figure 5, which gives SO_2 capture by the $Ca(OH)_2$ component of BLIS as a function of loading. Here, loading

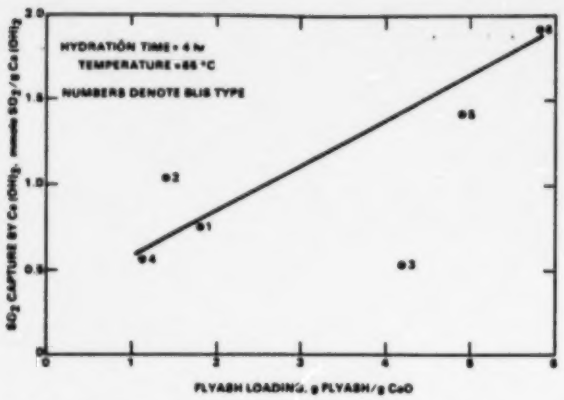
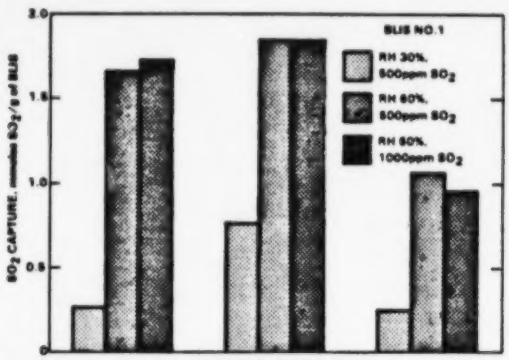


Figure 5. Effect of fly ash loading on the SO_2 capture by $Ca(OH)_2$ in BLIS.



TIME OF HYDRATION, HR	4	24	4
TEMPERATURE OF HYDRATION, °C	65	90	65
ADDITIVE, WT % $(NH_4)_2HPO_4$	3	0	0

Figure 6. Combined effect of conditions of hydration and exposure to SO_2 in the sand bed on the SO_2 capture by BLIS 1.

is defined as the ratio of insoluble solids to available CaO. The CaO and insoluble solids were determined by analyses described earlier. The general trend, as shown in Figure 5, was that SO_2 capture by BLIS increased with higher loading. BLIS 3 did not follow this pattern. On the basis of the total sorbent mass, SO_2 capture was about 1 mmol of SO_2/g for BLIS 1, 2, 4, and 6 and about 0.7 mmol of SO_2/g for BLIS 3 and 5.

Samples from the same sorbent batch used in the sand bed experiments for 500 ppm SO_2 and 60% relative humidity were tested at 500 ppm SO_2 and 30% relative humidity and 1000 ppm SO_2 and 60% relative humidity. The results in Figure 6 show the combined effect of humidity and SO_2 concentration on the SO_2 capture by BLIS 1. The general trend suggests that these samples were insensitive to the increase of SO_2 concentration from 500 to 1000 ppm. However, lowering relative humidity from 60 to 30% had a dramatically negative effect on SO_2 capture. Except for the sample hydrated at 90 °C for 24 h (which at 30% relative humidity and 500 ppm SO_2 yielded a SO_2 capture of 0.77 mmol of SO_2/g of sorbent), the other samples gave much lower SO_2 capture at 30% relative humidity than at 60%. For example, the SO_2 capture of the sample hydrated for 4 h at 65 °C dropped from 1.06 to 0.25 mmol of SO_2/g of sorbent at corresponding conditions. More SO_2 capture data are shown in Table III. The dramatic effect of relative humidity on SO_2 absorption by reactivated

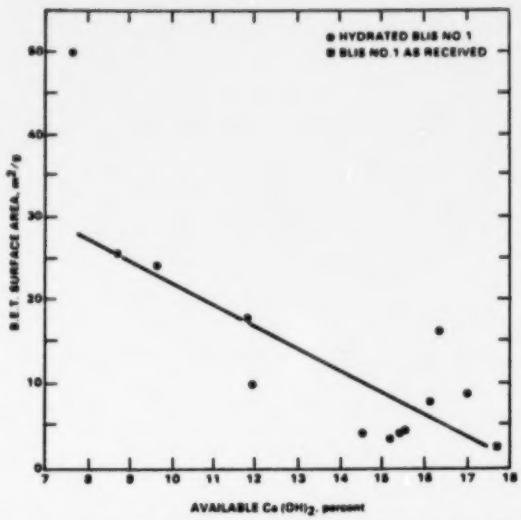


Figure 7. Effect of hydration on properties of solids (BLIS 1 hydrated under different time/temperature conditions).

BLIS is believed due to its hygroscopic character, with higher humidity promoting greater lime dissolution and enhancing the SO_2/sorbent reaction. Also, at low relative humidity, highly hydrated phases of the sorbent may contract and decrease the sorbent surface area available for contact with SO_2.

Possible Mechanism of SO_2 Capture. The data presented earlier showed that the reactivity of all six different BLIS samples was greatly improved after hydration. The surface area of the atmospherically hydrated samples increased severalfold, and highly hydrated crystals were detected with X-ray powder diffraction. During the hydration experiments, the available $Ca(OH)_2$ was tracked. The results (see Figure 7) are given in terms of the BET surface area as a function of available $Ca(OH)_2$ in the sample after hydration (see also Table III). Initially, BLIS 1 had 14.6% $Ca(OH)_2$ available and a surface area of 2.67 m^2/g. As the surface area of the hydrated BLIS increased via treatment, the available $Ca(OH)_2$ decreased. This decrease is explained by the $Ca(OH)_2$ combined with silica being digested from the BLIS and forming calcium silicates, which cannot be detected by the analysis for available $Ca(OH)_2$.

A significant change in surface area was evident when BLIS 1 was hydrated under different time/temperature conditions. The initial value for untreated BLIS 1 was 2.67 m^2/g, but the maximum surface area measured (after 24 h of sample hydration at 90 °C) was 50.86 m^2/g. It was observed that the surface area increased with both hydration time and temperature. For example, after 8 h of hydration it was 4.73 m^2/g for 25 °C and 25.84 m^2/g for 90 °C. Increasing time from 4 to 24 h at 65 °C resulted in the surface area growing from 7.95 to 24.57 m^2/g. The good correlation between the surface area developed and SO_2 capture by the sample is evident in Figure 8 for BLIS 1. Samples hydrated for 4 h with 1 or 3% (by weight) of $(NH_4)_2HPO_4$ gained reactivity (following significant increases in surface area) in a much shorter time than those hydrated without the additive (see also Table III).

The beneficial effect of increased surface area on the removal of SO_2 is dependent on the rate-limiting step. If SO_2 removal is controlled by the diffusion of SO_2 through the "ash" layer, increased surface area provides more gas–solid contact and, therefore, the ash formed in the initial steps of the reaction is spread over a larger surface

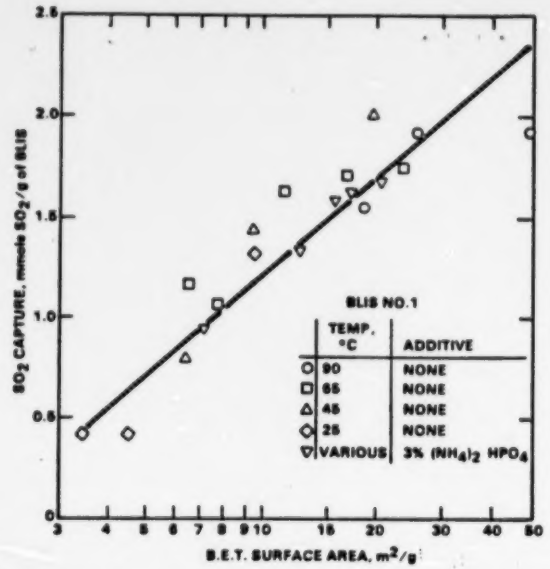


Figure 8. Correlation between surface area developed during hydration and SO_2 capture by BLIS 1 in the sand bed.

in a thinner layer. If SO_2 removal is controlled by the chemical reaction, the reactivity could also increase with higher sorbent surface area. More importantly, when the sorbent surface contains highly hydrated species, the water of hydration can be released upon contact with hot gas. This release provides moisture that may be necessary for SO_2 capture by $Ca(OH)_2$. Releasing the water of hydration could expose more pores, therefore creating new surface area.

Potential Application. The reactivated sorbents developed and studied in the bench-scale experiments reported here may make dry sorbent injection an attractive low-cost SO_2 control option. While the test procedure used appears more appropriate to dry sorbent injection into a duct carrying low-temperature flue gas followed by particulate collection in a baghouse, spray drying with the sorbent in slurry form and particulate collection via either a baghouse or an electrostatic precipitator may also be technically and economically feasible. However, as shown by limited in-house pilot plant testing on fly ash/lime sorbents, the hygroscopic nature of these sorbents limited the approach to saturation temperature to values somewhat above the minimum 10 °C used in lime spray drying for SO_2 control, but values more suited for acid gas control in municipal waste incinerators. It was also determined that spray drying of the activated fly ash/lime sorbents produced a less reactive product (larger particles and lower BET surface area) than did the vacuum filtering followed by oven or microwave drying. A similar behavior would be expected of reactivated BLIS. Further work is needed to evaluate reactivated BLIS and other advanced sorbents now being developed for spray drying application, as well as determining their technial and economic feasibilities at the pilot and demonstration scales.

Conclusions

From the above study, the following conclusions may be drawn:

(1) Reactivation of BLIS is possible and may be accomplished by the atmospheric hydration of dry solids under conditions permitting reaction of calcium with silica to form high surface area sorbents.

(2) New crystals ($CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}CaSO_4$ compounds) were found in hydrated BLIS samples.

(3) The amount of available $Ca(OH)_2$ detected by analysis decreases as the BET surface area and SO_2 capture increase.

(4) The surface area of hydrated BLIS increases with hydration time and temperature; SO_2 capture correlates well with surface area, increasing with increasing surface area.

(5) SO_2 capture with hydrated BLIS increases with the increasing ratio of fly ash to lime in the sorbent.

(6) The reactivity of hydrated BLIS is very sensitive to the relative humidity of gas, with SO_2 capture being enhanced by high relative humidity.

(7) Early pozzolanic reaction in the hydrated BLIS is probably responsible for the formation of highly reactive sorbent for SO_2 removal.

(8) A potential mechanism for enhancing SO_2 capture involves the increased particle surface area of the reactivated BLIS. This increased surface area, and possibly additional area exposed when water evaporates from the particle pores on contacting the hot gas, appears to be the basis for the enhanced reactivity of the reactivated solids.

Registry No. SO_2, 7446-09-5.

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